

## PATENT SPECIFICATION

NO DRAWINGS

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## COMPLETE SPECIFICATION

## Manufacture of Linear Polyesters

We, EASTMAN KODAK COMPANY, a Company organized under the Laws of the State of New Jersey, United States of America, of 343 State Street, Rochester, New York 14650, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the preparation of linear polyesters.

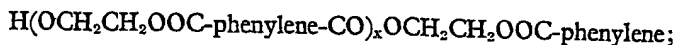
The preparation of polyesters by esterification of ester exchange and condensation is well known and described in Specification No. 578,079. In the case of poly-(ethylene terephthalate), for example, it is customary to react dimethyl terephthalate with a molar excess of ethylene glycol to form a low molecular weight polymer (i.e., prepolymer) and by-product methanol. After the methanol is nearly completely removed by distillation, the reaction temperature is raised and remaining ethylene glycol is removed by distillation. The reaction is then continued by maintaining the temperature of the reaction vessel until a polyester of the desired molecular weight is obtained. The molecular weight of the product may be high enough that the polyester can be used for forming films and fibres. Such a system, whether batch or continuous,

is known as a melt polymerization process. In accordance with such process, the polymerization can be continued until a polyester is obtained or the melt process may be stopped at some intermediate point to obtain a prepolymer, i.e., a polymer having a molecular weight of from about 2,000 to about 10,000 and having an intrinsic viscosity of about 0.1 to about 0.45. The Intrinsic Viscosity is measured at 25°C in a 60:40 mixture by weight of phenol and tetrachloroethane. This material can be stored and subsequently further polymerized by remelting and continuation of the melt process or, more advantageously, it may be crystallized, ground and subjected to solid phase polymerization either by batch or continuous processes.

It is known that the preparation of polyesters from a glycol and a dibasic acid is facilitated by the use of esterification catalysts and that polyesterification is a reversible, equilibrium reaction which may be exemplified as follows:



wherein, for poly(ethylene terephthalate) for example, R represents  $\text{CH}_3\text{OOC-phenylene}$ ,



$\text{R}^1$  represents  $-\text{CH}_3$  or  $-\text{CH}_2\text{CH}_2\text{OH}$  and  
 $\text{R}^2$  represents  $\text{HOCH}_2\text{CH}_2-$  or



The esterification catalysts which may be used in the preparation of polyesters, such as described above, include organic and inorganic [Pr

compounds of metals such as titanium, antimony, zinc, lead, calcium, lithium, combinations thereof, heretofore used by those

skilled in the art. The prior art, for example, discloses a great number of such catalysts, some of which are described in patents such as U.S. 2,465,319, U.S. 2,720,502 and U.S. 2,727,881. Specific catalysts heretofore known and which are used, include titanium tetrabutoxide or tetraisopropoxide, titanium dioxide, zinc acetate, zinc acetyl acetonate, lead oxide, calcium oxide, lithium ethoxide, antimony trioxide, antimony hydroxide, antimony salts such as antimony sulphate, antimony acetate and antimony chloride, and manganese oxides.

The present invention relates specifically to those polyesterification processes that involve the use of an antimony polyesterification catalyst and one or more zinc salts, such as zinc acetate.

While the use of an antimony polyesterification catalyst is desirable for several reasons which are well known to those in the art, such use heretofore often resulted in special problems, apparently because under certain conditions (for example, due sometimes to the presence of reducing type stabilizers such as the trialkyl phosphites as described in Specification No. 770,531) some of the antimony catalyst was reduced to metallic antimony, which not only caused a generally undesirable gray colour to be imparted to the polyester product, but also caused filter plugging and even resulted in excessive film specks and fibre breakage, and/or discolouration when the superpolyester product was converted into such end-use materials. Efforts heretofore to cure these problems consistently (caused by the presence of metallic antimony), for example, by oxidizing the metallic antimony to an oxidized state (such as antimony oxide, in which form the antimony is both colourless and soluble in the polyester system) by simply passing oxygen over or through a heated bed of polyester material containing the troublesome metallic antimony, were unsuccessful.

It has now been discovered that these problems can be solved consistently, not simply by oxidizing the metallic antimony, per se; but by the surprising expedient of oxidizing a non-antimony bearing material concurrently with the metallic antimony, apparently at the sites of the tiny specks of antimony metal in the effected polymeric materials. For some presently unexplainable reason, the desired oxidation of metallic antimony can apparently only be carried out in conjunction with the oxidation of another component, which other components preferably contains no antimony. Since in the processes which the present invention is concerned it is necessary to prevent the effected polymeric material from melting, the "oxidizable material" (that is oxidized concurrently with the metallic antimony in the processes of this invention) must be of the type that can be oxidized in the presence of oxygen at a tem-

perature between 100°C. and the melting point of the particular polyethylene terephthalate being treated (preferably at a temperature between 160°C. and 210°C.). The "oxidizable materials" that can be used in the present processes are acetaldehyde, ethylene glycol, and ammonia. These oxidizable materials are volatile at ordinary process temperatures in the inert gas streams (which are preferably largely nitrogen gas) used to blanket the polyester during the latter stages of the polymerization processes. At least 0.005 weight percent (and preferably at least 0.05 weight percent) of the volatile oxidizable material should be present in the inert gas stream which is in intimate contact with the polyester during at least a portion of the time during which the polyester is exposed to temperature above 150°C in order to convert the troublesome metallic antimony to the oxidized state. If desired, up to 5 weight percent or more of the oxidizable material, based on the weight of polyesterification reactants, can be present in the gas stream, although generally, no more than 1 weight percent of these materials need be utilized in order to attain substantially complete conversion of the undesired metallic antimony of the oxidized state.

According to the present invention there is provided a process for the manufacture of linear polyethylene terephthalate comprising:

- (1) reacting together in a metal phase ethylene glycol and dimethyl terephthalate, in the presence of an antimony catalyst and a zinc salt, to form a molten prepolymer having an intrinsic viscosity from 0.2 to 0.5;
- (2) adding a reducing stabilizer to the molten prepolymer and thereafter cooling the molten prepolymer to solidify it;
- (3) grinding the solidified prepolymer to form a particulate solid having a particle size less than 600 microns;
- (4) in a solid phase polymerization step increasing the intrinsic viscosity of the polyester by heating the particulate solid prepolymer at a temperature greater than 150°C but below its melting point in the presence of an inert gas atmosphere until the intrinsic viscosity of the polyester is greater than 0.5, characterised in that, the inert gas atmosphere contains at least 0.005 weight percent of one of the oxidizable materials ammonia, acetaldehyde or ethylene glycol, and from 1 to 6 volume percent of oxygen for at least ten minutes and until all the metallic antimony present is converted to an oxidized state.

The oxidizing agent that is used in the successful practice of this invention is oxygen

gas (in admixture with the inert environmental gas) at levels of 6 volume percent of the inert gas stream or atmosphere.

For conversion of most of the metallic antimony to the oxidized state, generally the oxidizing conditions set out above should be maintained until the desired result is accomplished; this is generally for at least 10 minutes, and preferably for at least 20 minutes, and up to 120 minutes or more, depending on several factors. Generally, the rate of the desired oxidation increases with increasing temperatures, and it is usually desirable to stop the oxidation, preferably by reducing the amount of oxygen in the gas stream environment to below 1 volume percent, fairly quickly after the desired amount of oxidation (of metallic antimony) has been accomplished. This can readily be accomplished by simply purging the system with large volumes of inert gas, or by chemically removing the oxygen from the environmental gas stream, or by any of a number of other means known to the ordinary skilled chemist. The main reason for limiting the amount of time the oxidizing conditions are maintained in these processes is to prevent or minimize deterioration of the polyester, itself (i.e., to thereby prevent the development of discolouration caused by oxidation in the end product superpolyester).

The basic polyesterification processes to which this invention relates are well known to those in the art and for this reason need not be extensively detailed here. The processes entail, for example, the use of a total polyesterification catalyst concentration of from 10 to 3000 parts per million, based on the weight of the reactants, although the usual range is from 20 to 1000 parts per million, and preferably from 50 to 500 parts per million. Of this, the total antimony polyesterification catalyst concentration at the beginning of the polyesterification reaction is generally from 50 to 500 ppm. based on the weight of antimony metal, and preferably within the range of from 100 to 250 ppm.

The polyethylene terephthalate prepared according to the invention has a number average molecular weight of 15,000 to 100,000 and an intrinsic viscosity in a mixture of 60% phenol and 40% tetrachloroethane at 25°C of at least 0.50 and melting at from 180° to 350°C., and preferably having been prepared as follows:

(1) Heating from 1 to 3.5 mole proportions of ethylene glycol with one mole proportion of dimethyl terephthalate under conditions such that at first there is removed substantially all of the methanol corresponding to the ester and subsequent thereto there is removed most of the excess of ethylene glycol whereby an intermediate polyester prepolymer having an intrinsic viscosity of from 0.2 to 0.5 is obtained.

(2) Comminuting and "prepolymer" to form solid particles having an average particle diameter below 600 microns and then

(3) In an enclosed polymerizing zone wherein at least 5 percent of the volume is occupied by said particles, heating to at least 150°C but below the melting point of the prepolymer (between 160 and 210°C) in the presence of a solid phase polyester polymerization catalyst and an inert gas at atmospheric pressure which flows through said zone at from 0.01 to 1000 ml. of inert gas per minute per gram of said particles, any of the particles more than 5mm. from the surface being agitated into contact with said inert gas, whereby a substantially colourless superpolyester having an intrinsic viscosity of at least 0.5 and generally greater than 0.6 is obtained within ten hours or less of commencing said heating in the polymerization zone, the intrinsic viscosity being at least 0.3 unit greater than for the prepolymer and usually 0.4 or more units greater.

The detailed aspects of the described process will be readily apparent to those having ordinary skill in this art since the preparation of polyesters such as poly(ethylene terephthalate) which are fibre and film forming has now been understood by such persons for a good number of years and the literature is quite extensive in regard to this subject matter. Such processes are described in Specification No. 1,041,853.

The inert gas which can be employed in accordance with the process of this invention can be any of those which are ordinarily employed in the handling of polyesters in accordance with the prior art. Such inert gases include nitrogen, carbon dioxide, hydrogen, helium, propane, mixtures of such gases and other related gases.

Phase 1 as set forth hereinabove can be conducted as a single operation or can be divided into two separate steps. In the latter case it is sometimes preferable to perform the initial ester interchange between the ethylene glycol and the dimethyl terephthalate components in a batch reactor or in a column equipped with plates. Of course other apparatus can also be employed. The reactor or column is preferably equipped with a reflux device such as a packed column which returns to the reaction zone any of the glycol which might otherwise be lost during the ester interchange step. The methanol (originally part of the dimethyl terephthalate ester starting material) is removed from the ester interchange zone. The second step of this first phase can then be accomplished preferably by heating the ester interchange product in a batch reactor or some other suitable reaction vessel so as to remove a substantial proportion of the ethylene glycol in excess of that required to form the polyester. This step is normally accomplished under reduced pres-

sure which facilitates the removal of the glycol. During this step, "prepolymer" is usually formed.

5 The second phase of the described process, involving the comminuting of the prepolymer, can be accomplished in any convenient manner as long as the particles produced come within the size requirements set forth. According to one method the prepolymer can be cast as a thick sheet of the product of phase 1 and 10 allowed to cool slowly whereby it can be readily broken into small pieces. These pieces can then be ground in any of the commonly available grinding machines so as to produce particles of the appropriate sizes. The slow cooling of the prepolymer as a thick sheet facilitates its developing a crystalline form which makes subsequent comminution relatively easy. It has been observed that it is generally during this phase of the generic polyesterification processes that most of the objectionable metallic antimony is apparently 20 formed, when a material having a reducing stabilizer, such as, for example, phosphorous acid, a monoalkyl phosphite or a trialkyl phosphite, is present in the reaction mass. Crystallization with regard to the material used to form the comminuted particles is not only useful in preparing the comminuted particles, 30 but it is also advantageous in accomplishing the final polymer build-up.

If it is desired to enhance the crystallinity of the particles of prepolymer to be used as set forth in phase 2, this can be accomplished 35 by contacting the particles with an organic volatile liquid compound which is allowed to permeate the particles for a period of time sufficient to permit a high order of crystallization to be achieved. The particles containing the volatile organic liquid can then be heated at an adequate temperature to evaporate the liquid and leave the particles dry. If necessary, the dried particles can be subjected to further mechanical action to cause 40 them to have the appropriate sizes.

45 In preparing the solid particles of prepolymer it is generally preferred to employ a prepolymer which does not have an intrinsic viscosity any greater than 0.4—0.45.

50 The solid phase operation is conducted in an enclosed polymerising zone wherein at least five per cent of the volume is occupied by the particles. Such a zone can be a horizontal tube, upright cylinder or any other chamber through which inert gas can be 55 conveniently moved across the surface of the particles and/or around the particles.

60 There is no clear cut range of flow rates for the inert gas passing over the surface or through (around) the prepolymer particles since the effectiveness of the flowing gas depends to a considerable extent on the geometry of the polymerising zone. However, it appears that a range of from 0.01 to 1,000 ml. of 65 inert gas per minute per gram of the solid

particles cover about as much variation in flow rate as appears ordinarily practicable. An excessively high flow rate will obviously be economically wasteful since it will require employment of more heat in order to maintain the powder buildup conditions in the polymerising range of temperatures.

70 The particles in the polymerising zone can be heated initially at from 40° to 80°C. below the melting point of the prepolymer. The most effective polymerisation temperature depends upon the nature of the polyester and upon the type of catalyst employed. Generally the initial polymerisation temperature is 75 200—260°C. although higher and lower temperatures are operable such as 180—425°C., depending upon the melting behaviour of the polyesters.

80 According to one preferred method of practicing this aspect of the present invention, the prepolymer is finely ground to form solid particles in the 40 to 70 U.S. Standard mesh size (420—210 microns) which are heated in a horizontal or vertical glass or metal tube at the polymerisation temperature in the presence of a standard powder build-up (i.e. 85 polymerisation or polyesterification) catalyst until the desired increase in the molecular weight of the polyester is obtained. The degree and rate of molecular weight buildup of the prepolymer is somewhat dependent upon the catalysts used, the particle size, the polymerisation temperature, the rate of flow of the inert gas over the bed of prepolymer, the thickness of the bed of prepolymer, and 90 the diameter of the reaction tube or bed.

95 The particle size of the prepolymer is ground to from 40 and 70 mesh, U.S. Standard sieves, for the "fluidized bed" technique used in phase 3; although larger or smaller particles may be employed within the limits set forth above. Larger size particles tend to slow down the rate of molecular weight buildup. The presence of a very high proportion of particles passing 200 mesh (such as about 10% or more) is undesirable since such particles tend to be picked up by the moving gas and carried away. Generally, however, the average particle size (diameter) 100 of the prepolymer is below 600 microns.

105 One way for accomplishing the powder buildup is to conduct the polymerisation in apparatus which maintains the solid particles in a fluidized condition. Such apparatus is well known in the cement making and the powdered coal handling industries, as well as elsewhere. For example, an upright cylindrical fluidized blender can be employed to suspend and agitate particles with hot inert gas while the walls of the blender are maintained at a temperature adequate to heat the particles to accomplish the polymerisation. Additional prepolymer can be added to such a blender on a continuous basis and "build up" particles can be removed as desired. 110 115 120 125 130

Another device is to use a somewhat tilted hollow reaction tube which may have a corrugated cross section and which can be rotated around its longitudinal axis. Prepolymer powder can be introduced into the higher end of the tube and inert gas passed through the tube, preferably through the opposite end. The tube can be designed so that the particles of prepolymer will remain within the tube for a desired period of time while the tube is being rotated. The particles then move downwardly according to the degree of slope of the tube. By using such a rotating tube apparatus the particles of "built up" polymer have a substantially uniform intrinsic viscosity and are quite advantageously employed for products where a relatively narrow range of molecular weights is desirable, such as in the manufacture of photographic film base or fibres.

The temperature at which the polymerisation during the powder buildup is conducted should not be so high as to cause non-frangible agglomeration of the particles during the solid phase polymerisation. The maximum temperature which can be employed will be determined by the precise conditions employed. By the "avoidance of nonfrangible agglomeration", it is meant that the material should not fuse together completely, but should remain in a form such that it is quite frangible and can readily be broken up after the polymerisation has been completed. As has already been pointed out, the desired agitation during "phase 3" can be accomplished by means of the inert gas (which can be heated) being passed through the particles of the solid polymer as in the case of fluidisation. Agitation can also be accomplished by stirring the particles in an enclosed polymerising zone or by other means such as when the previously described rotating tube is used. Agitation is especially important if the depth of the polymer bed is 5 mm. or more. A static bed can be used when the depth of polymer is less than 5 mm.; preferably no more than 3 mm. Of course static beds having depths greater than 5 mm. could be used with some adverse effects upon the results achieved.

When a "bed" of prepolymer is employed in a substantially horizontal (rotatable) tube, the thickness of the bed can be between 1 percent and 25 percent of the diameter of the reaction tube. Such a bed can be established within the larger sizes of reaction tubes by placing it upon a substantially horizontal and flat supporting surface across the lower half of the tube. Such a bed would then constitute at least 5 percent of the volume of the polymerising zone above the supporting surface. The maximum volume of the bed in the zone in such a case would be limited by the practical problems associated with the flow of inert gas over the bed.

In cases where the polymerising zone involves apparatus which fluidises the particles, it is possible for the fluidized material to occupy a fairly major proportion of the total polymerising zone. The same would be true when other devices are being used for agitating the prepolymer particles and passing the inert gas through the agitated mass. In such cases, much of the volume of the polymerisation zone is filled with the gas used to fluidise the particles and such gas occupies the interstices between the particles.

It is obvious that there are numerous variations of the process of this invention among which would be the employment of mixtures of prepolymer particles using different prepolymers.

The practice of this invention provides a rapid, efficient process for obtaining colourless fibres and film forming polyesters having exceptionally high molecular weights by simple economical means. The process of this invention is well adapted to continuous operation.

This invention can be further illustrated by the following examples, although it will be understood that these examples are merely illustrative, and are not intended to limit the scope of the invention unless otherwise specifically indicated. In the following examples, all parts given are by weight unless otherwise specified.

The following Preparation I illustrates one of the conventional procedures for manufacturing poly(ethylene terephthalate) prepolymer in which the formation of troublesome metallic antimony is evident.

#### PREPARATION I

Into a conventional stainless steel reaction vessel fitted with a stirrer and a condenser-collector system (to collect methanol from vapours evolved during the ester interchange) are charged 100,000 parts of molten dimethyl terephthalate, 65,000 parts of ethylene glycol, 465 parts of zinc acetate and 695 parts of antimony trioxide. The zinc and antimony compounds are poly-esterification catalysts. The resulting mixture (initially at a temperature of 150°C.) is heated gradually, over a period of four hours, to a temperature of 255°C. During this time, evolved methanol is continually withdrawn from the reaction zone. When the temperature has reached 255°C., removal of ethylene glycol, via distillation under reduced pressure is begun. After 25,000 parts of ethylene glycol have been removed [leaving relatively pure low molecular weight poly(ethylene terephthalate)], then the temperature of the reaction mass is increased gradually (over about 1 hour) to 275°C. Thereafter, this temperature is maintained while the pressure in the reactor is gradually reduced to about 2mm-Hg. This low pressure is maintained, then, for an addi-

TABLE I

Treatment of Grey Prepolymer in Nitrogen Gas Atmosphere

Example	Additive Used	Amount	O <sub>2</sub> % Level	Time	°C	Remarks
I	acetaldehyde	0.1	3	30	204	white
II	ethylene glycol	0.18	1	105	218	white
III	ethylene glycol	0.2	2	55	205	white
IV	ethylene glycol	0.8	1	105	218	white
V	ethylene glycol	16	1	25	175	white

5 It should be noted at this point that under certain circumstances the polyesterification reaction itself can serve as the source of the ethylene glycol "oxidizable material" to accomplish the necessary oxidation of this invention. Under these circumstances, special efforts should be made to retain these materials in the reaction system for a time sufficient to result in the desired reaction (in the presence of sufficient oxidising agent, of course).

## WHAT WE CLAIM IS:—

15 1. A process for the manufacture of linear polyethylene terephthalate comprising:

- 20 (1) reacting together in a melt phase ethylene glycol and dimethyl terephthalate, in the presence of an antimony catalyst and a zinc salt, to form a molten prepolymer having an intrinsic viscosity from 0.2 to 0.5;
- 25 (2) adding a reducing stabilizer to the molten prepolymer and thereafter cooling the molten prepolymer to solidify it;
- (3) grinding the solidified prepolymer to form a particulate solid having a particle size less than 600 microns;
- 30 (4) in a solid phase polymerization step, increasing the intrinsic viscosity of the

polyester by heating the particulate solid prepolymer at a temperature greater than 150°C but below its melting point in the presence of an inert gas atmosphere until the intrinsic viscosity of the polyester is greater than 0.5, characterised in that, the inert gas atmosphere contains at least 0.005 weight percent of one of the oxidizable materials, ammonia, acetaldehyde or ethylene glycol, and from one to six volume percent of oxygen for at least ten minutes and until all of the metallic antimony present is converted to an oxidized state.

2. The process as claimed in claim 1 wherein the reducing stabilizer is phosphorous acid, a monoalkyl phosphite, a dialkyl phosphite or a trialkyl phosphite.

3. The process as claimed in any of the preceding claims wherein the inert gas atmosphere is predominantly nitrogen.

4. Processes of manufacturing linear superpolyesters as claimed in claim 1 as herein described.

5. Linear superpolyesters whenever made by the method of any of the claims 1 to 4.

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